

Isolation and Structural Determination of {(1,1,2,2-Tetracyano-1,2-ethanediyl)bis[imino(cyanomethylene)]bis(cyanamide) ion(2-), [C₁₂N₁₂]²⁻, a New Cyanocarbon

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The oxidative degradation of [N(PPh₃)₂]₃[Mn^{III}(CN)₆] leads to the isolation of the unprecedented [C₁₂N₁₂]²⁻ dianion, which is characterized by single-crystal X-ray diffraction and spectroscopic techniques.

The study of cyanocarbons has led to several new classes of compounds based upon reduction of the nitrile triple bond.¹ In an attempt to prepare [Mn^{IV}(CN)₆]²⁻, oxidation of [N(PPh₃)₂]₃[Mn^{III}(CN)₆] led to the isolation of light-yellow crystals with anomalous infrared absorptions at 2199 and 2176 cm⁻¹, assigned to ν(CN) and a very strong unassigned absorption at 1559 cm⁻¹. The absorptions below 2200 cm⁻¹ were too low in frequency to be assigned to a nitrile, and were thought to be associated with a new cyanomanganate. Crystals

isolated from MeCN were suitable for X-ray diffraction and the structure of the unprecedented {(1,1,2,2-tetracyano-1,2-ethanediyl)bis[imino(cyanomethylene)]bis[cyanamide] ion(2-), **1**, was determined.^{†,‡} The anion [C₁₂N₁₂]²⁻ is centrosymmetric about the midpoint of the C(3)–C(3') bond, Fig. 1. Except for the C(3) cyano groups the dianion is planar with deviations from the plane ranging from 0.0012 to 0.0715 Å and averaging ±0.023 Å. The chemically equivalent C≡N bond distances (1.138 Å) are comparable to the plethora of nitrile groups structurally determined. The 1.577(10) Å central sp³–sp³ C–C bond length is longer than the conventionally accepted value for the 1.54 Å and is significantly (0.09 Å) longer than the sp²–sp² C–C single bond in C₄(CN)₆ (1.487 Å).² The sp³–sp C(3)–CN bond distances average 1.508 Å while the sp²–sp C(2)–CN distance is 1.449 Å and the CN single bond [C(3)–N] is 1.403 Å. The delocalized CN bonds range from 1.314(7) to 1.342(7) Å for the C(2)–N bonds, and the short C(1)–N(2) bond (1.331 Å) reflects some double bond character. The significant differences in the C(2)–N bonds is a consequence of the asymmetry about C(2).

The IR absorptions at 2199 and 2176 cm⁻¹ are consistent with [CN]₆²⁻ [ν(CN) at 2165 cm⁻¹^{3a}] and [CN]₈²⁻ [ν(CN) at 2180 cm⁻¹^{3b}] while the previously unassigned strong absorption at 1559 cm⁻¹ is due to the C=N bonding. [N(PPh₃)₂]₂[C₁₂N₁₂] has a λ_{max} at 34 725 cm⁻¹ (ε = 24 000 dm³ mol⁻¹ cm⁻¹) due to the conjugated chromophore. Absorptions at higher energy are attributed to the [N(PPh₃)₂]⁺ cation.

The oxidative decomposition of [Mn^{III}(CN)₆]²⁻ undoubtedly leads to the formation of CN⁻ and CN• which reacts in a complex manner to form [C₁₂N₁₂]²⁻ which crystallizes as the [N(PPh₃)₂]⁺ salt. CN• dimerizes to form cyanogen and the reaction of cyanogen with CN⁻ leads to many products of which the best characterized is 1-*H*-imidazo[1,5-*b*]-*s*-2,5,7-tricarbonitrile, [C₇N₇]⁻, **2**.⁴ Reduction of **2** or cyanogen leads to poly(cyanogen), C_nN_n.⁵ Hence, isolation of [C₁₂N₁₂]²⁻ and **2** suggests that many unusual products as a consequence of C–C and CN, and in the case of **2**, N–N bond formation can be formed, via the reaction of cyanogen and CN⁻.

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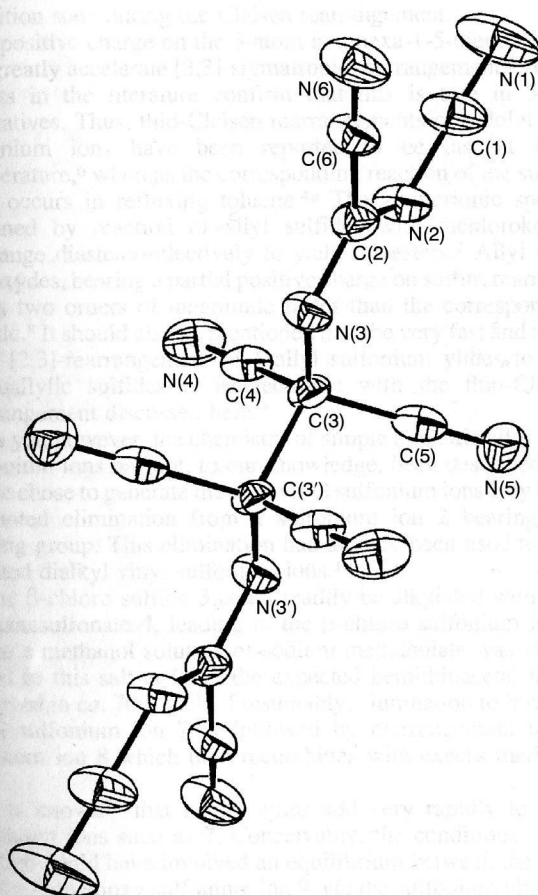
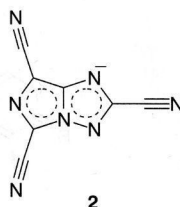
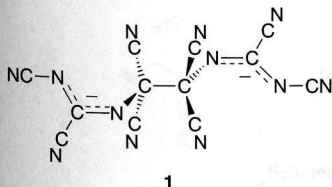


Fig. 1 Structure and labelling diagram of [C₁₂N₁₂]²⁻



Footnotes

† Elemental analysis: Found: C, 72.15; H, 4.50; N, 13.95. Calc. for C₈₄H₆₀N₁₄P₄: C, 72.60; H, 4.35; N, 14.10%.

‡ Crystal data for **1**: C₈₄H₆₀N₁₄P₄, *M* = 1389.4, monoclinic, space group *P*2₁/*n*, *a* = 12.155 (1), *b* = 19.789 (2), *c* = 15.751 (2) Å, β = 104.52 (1)°, *U* = 3667.76 Å³, *F*(000) = 1444, *Z* = 2, *D*_c = 1.258 g cm⁻³, λ = 1.54184 Å, crystal size 0.30 × 0.20 × 0.13 mm, *T* = 18 °C, 2θ_{max} = 98°, *R*_w (on *F*) [*R* (on *F*)] = 0.0519 (0.0468), for 3839 unique reflections with *I* > 3σ(*I*). Data was collected on a Syntex P1 diffractometer and the crystal structure solved using MOLEN software distributed by Enraf Nonius. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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